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A catalytic surface reaction model *

Maury Bramson

Department of Mathematics, University of Wisconsin, Madison, WI 53706, United States

Claudia Neuhauser

Department of Mathematics, University of Southern California, DRB 306, 1042 West 36th Place, Los Angeles, CA 90089-1113, United States

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Abstract

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The purpose of this paper is to describe a two-dimensional catalytic surface reaction between two reactants, M and P_n: $P_n + nM \to nPM$, where P_n is a polymer consisting of n identical atoms and M is a monomer. A classical example is the oxidation of carbon monoxide. In this case, $M = CO$ and $P_n = O_2$. We will consider the case where n, the polymer size, is large. Detailed proofs will be given in a forthcoming paper.

Keywords: Continuous time Markov process, catalytic surface reaction.

1. Introduction

We consider a simple model which describes a reaction between two components on a catalytic surface. The surface is given by the two-dimensional integer lattice. The components are adsorbed on vacant sites of the catalytic surface. One of the components is a monomer M which requires only a single vacant site for adsorption. The other component is a polymer P_n, consisting of $n = N^2$ identical atoms arranged in a square of length N, which requires a vacant $N \times N$ square on the surface for adsorption. After adsorption, the polymer disassociates into N^2 polymer atoms, each of which occupies a single site. Monomers and polymer atoms are assumed to react with each other instantly when they are within a given distance.

We model this reaction as a continuous time Markov process in which the state at time t is

Correspondence to: Prof. M. Bramson, Department of Mathematics, University of Wisconsin, Madison, WI 53706, United States.

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$\xi_t : \mathbb{Z}^2 \to \{0, 1, 2\}$ (that is, each site in $\mathbb{Z}^2$ is assigned the value 0, 1 or 2). We interpret 0 as being vacant, and 1 (respectively 2) as being occupied by a monomer (respectively polymer atom). The dynamics consist of three parts: adsorption, reaction between different components and desorption. The rules are as follows.

(i) 0's turn into 1's at rate 1, i.e., vacant sites become occupied by monomers at rate 1.

(ii) $N \times N$ squares of 0's turn into $N \times N$ squares of 2's at rate λ, i.e., $N \times N$ squares of vacant sites are occupied by polymers at rate λ. Polymers disassociate into single polymer atoms upon landing.

(iii) If $\xi_t(y) = 1$ and $\xi_t(x) = 2$ for some $x, y \in \mathbb{Z}^2$ with $\| x - y \|_\infty \leqslant R$, then both x and y are immediately vacated.

Here, $\| x \|_\infty \leqslant R$ means $\sup_i | x_i | \leqslant R$. Rules (i) and (ii) describe the adsorption mechanisms, rule (iii) describes the reaction between the components and desorption of the product. If a monomer is adsorbed and can react with more than one polymer atom (or vice versa), we choose one such atom at random. Consequently, a monomer reacts with only one polymer atom. The range R will be a function of N, the polymer length.

We investigate this model for N large. As we will see, the system exhibits different behavior depending on whether the range is large or small compared with the polymer size.

2. Oxidation of carbon monoxide

We first describe the original model which motivated this investigation. This model was introduced by Ziff et al. in [12]. They considered the chemical reaction between oxygen O_2 and carbon monoxide CO on a catalytic surface, a reaction which is important in automobile emission control. The catalytic surface is again represented by the two-dimensional integer lattice $\mathbb{Z}^2$. In the first step of the dynamics, the reactants are adsorbed on the surface. CO requires a single vacant site, whereas O_2 requires two adjacent vacant sites to adsorb. O_2 disassociates into two single O atoms upon adsorption. Adjacent CO molecules and O atoms react instantly to form CO_2, which immediately leaves the surface. The relative concentration of the O_2 and CO molecules in the gaseous state before adsorption is kept fixed. Ziff et al. observed interesting steady state behavior and two types of phase transitions. If the ratio of O_2 to CO in the gaseous phase is high, oxygen poisoning occurs, that is, the integer lattice will eventually become completely occupied by oxygen atoms and the reaction ceases. If the ratio is low, carbon monoxide poisoning occurs. For intermediate concentrations of oxygen and carbon monoxide, they found a reactive state in which both components occupy a positive fraction of the surface and for which the reaction persists (that is, the components coexist). Their computer simulations strongly suggest that the phase transition between the oxygen poisoned state and the reactive state is continuous, whereas the transition between the reactive state and the carbon monoxide poisoned state is discontinuous.

Their paper was followed by a series of nonrigorous papers in the physics literature (see, e.g., [4,8,10]). There are very few rigorous results on catalytic surface reaction models. A simplified model in which oxygen requires only a single vacant site for landing was studied in [9]; this result was extended in [11]. Durrett and Swindle [7] have investigated the original model of Ziff et al. under the additional assumption that the reactants move at a high rate on the surface.

3. The case of large polymers

We study the behavior of the model when the polymer size is large. We will see that the behavior depends on how large the range of the interaction is relative to the polymer size. From now on, polymers are $N \times N$ blocks which are adsorbed at rate λ on vacant $N \times N$ squares; N will be large. Monomers are adsorbed at rate 1 on vacant sites. The range of interaction is R, which depends on N.

Before we state our results, we define the following sets of initial configurations. Let Ξ_1 (respectively Ξ_2) be those configurations which at time $0+$ still have, with probability 1, infinitely many monomers or vacant sites (respectively infinitely many $N \times N$ squares not containing any monomers). Set $\Xi = \Xi_1 \cap \Xi_2$. Note that $\xi_0 \in \Xi_1$ rules out the case where the initial configuration has infinitely many vacant $N \times N$ squares but is otherwise completely filled with polymers. (For $\lambda = \infty$, this would result in an immediate polymer poisoning of the surface.)

The first theorem shows that monomer poisoning occurs when the range of interaction is small relative to the polymer size.

Theorem 1. *Let $R = \epsilon N$ with N large. There is an $\epsilon_0 > 0$ so that for $\xi_0 \in \Xi_1$ and $0 < \epsilon \leqslant \epsilon_0$, the polymers die out locally with probability 1 for all $\lambda \geqslant 0$.*

It is perhaps somewhat surprising that coexistence cannot occur for large polymers no matter how large λ is, since this behavior differs from that exhibited in the literature (always for small N).

The behavior is more complex when the range is large relative to the polymer size. This is the content of the next theorem.

Theorem 2. *Let $R = mN$ with N large. There is an $m_0 > 0$ so that for $m \geqslant m_0$,*

(i) *if λ is sufficiently large, coexistence occurs with probability 1 when starting from any initial configuration $\xi_0 \in \Xi$;*

(ii) *if λ is small, the polymers die out locally with probability 1 when starting from any initial configuration $\xi_0 \in \Xi_1$.*

We remark that there is no obvious monotonicity in the system which shows that decreasing λ implies a decreasing density of polymers. Therefore, Theorem 2 does not imply the existence of a critical λ_c at which the behavior of the system changes from monomer poisoning to coexistence. However, this does not prevent us from making the following conjecture.

Conjecture. *Let ξ_0 be a translation-invariant initial configuration in Ξ. If R/N and N are sufficiently large, then there exists a critical $\lambda_c \in (0, \infty)$ such that*

$$\lambda_c = \begin{cases} \inf\left\{\lambda\colon \lim_{t\to\infty} P(\xi_t(0) = 2) > 0\right\}, \\ \sup\left\{\lambda\colon \lim_{t\to\infty} P(\xi_t(0) = 1) = 1\right\}. \end{cases}$$

As indicated in the Abstract we do not give proofs here. However, we present a brief description of the main ideas. All the proofs are based on renormalization, by now, a fairly standard technique in particle systems (see, e.g., [1,2,6]).

For the proof of Theorem 1, we tile the plane into $L \times L$ squares where $L = \frac{2}{5}N$. We call such squares *occupied* if they contain at least one monomer. We call an $L \times L$ square *protected* if all of its eight nearest neighbors (in the L^∞ norm) are occupied. The choice of L implies that adsorbing polymers cannot intersect protected squares. The key idea is that before an $L \times L$ square is completely vacant, monomers will, with high probability, land and remain there (without reacting with a polymer atom). These monomers then block polymers from landing in protected squares; some monomers will, with high probability, also be adsorbed in neighboring squares, thereby creating more protected squares. Protected squares will then typically "fill up" with monomers, which causes the polymers within range R to desorb. This procedure continues, with neighboring squares continually being invaded by monomers. Thus, comparison with a growth model (e.g., biased voter model) shows that a solid blob of occupied squares has a positive probability of growing indefinitely.

The proof of Theorem 2(i) consists of two parts: to prove coexistence for R/N, N and λ sufficiently large, one needs to show that neither monomers nor polymers can poison the lattice. It is not hard to see that monomers cannot take over. For this, we will tile the lattice into $N \times N$ squares and call a square *occupied* if it does not contain any monomers. Suppose that a given square is occupied. A monomer can only remain on the lattice if there are no polymers within range R. Since the range is large relative to the polymer size, there will be enough space for polymers to be adsorbed and react with monomers. If λ is sufficiently large, then with probability close to 1, repeated adsorption of polymers will remove all monomers within range R of this square. This creates further occupied squares. Proceeding in this manner and comparing the set of occupied squares with oriented percolation, it follows that occupied squares will percolate.

For the other half of (i), we still need to show that polymers cannot take over. The proof is rather complicated. It is based on another renormalization argument. The renormalization is given by $L \times L$ squares where $L \in (\frac{1}{3}R, \frac{1}{2}R)$. One defines certain good events relating to squares, and shows that if the square centered at the origin is good at time 0, then, with probability close to 1, all four adjacent squares, centered at $(\pm \frac{1}{2}L, 0)$ and $(0, \pm \frac{1}{2}L)$, will be good at some fixed time T. Comparison with an appropriate supercritical oriented percolation process will then imply (i). The key idea is to keep track of the minimal number of polymer atoms that need to be removed before a square can be completely filled by polymer atoms. Call this quantity K. Then K can only decrease by one each time but can take large jumps up (depending on where monomers/polymers are adsorbed). We call a square *good* if K is sufficiently large. The proof relies on the fact that if K is not too large, then for at least a fixed proportion of the polymer atoms, the surrounding $\frac{2}{3}N \times \frac{2}{3}N$ square is completely filled with polymer atoms as well. Before K can decrease to 0, it will therefore be the case that except for an exponentially small probability, one of these "surrounded" polymer atoms will be removed. This then results in a sharp increase of K. Repeating this reasoning, it follows that K will, with high probability, remain large, and thus the square remains good for at least T units of time.

The proof of Theorem 2(ii) is considerably less involved. Intuitively, the result is quite clear: if polymers are adsorbed at a rate much smaller than N^{-2}, then the monomers must take over. There are, nonetheless, a few technical difficulties. One approach is to again compare the process with oriented percolation. In this case, a result from [5] on oriented percolation suffices.

More details will given in a subsequent paper [3].

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